

# Statistical Theory of Associating Polymer Solutions: Interfacial Properties

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ABSTRACT: The interfacial structure formed in thermoreversible associating polymer solutions is studied within the density functional approach based on Flory's arguments of tree-like configurations of cluster associations. The unique characteristics of the interfacial region can be described in terms of the monomer density along the interface. For a certain value of the association parameter, which controls thermoreversible chemical reaction between associating functional groups, the density profile is not smooth and undergoes a sudden jump at the point where the number of bonded functional groups is small. Analytical expression for the interfacial tension is given and results of numerical calculations are presented.

## 1. Introduction

The systems containing molecules capable of forming thermoreversible chemical bonds with each other are of significant interest from both fundamental and practical points of view. These types of systems are often referred to as weak gels<sup>1</sup> because the association between molecules under certain physical conditions, in particular lowering the temperature, leads to the formation of a thermoreversible infinitely large cluster (network or gel). At higher temperature, the molecules only form small, separated clusters of finite size, in the so-called "sol" solution.

The thermodynamical properties of weak gels have been modelled previously with various theoretical approaches and approximations.<sup>2-7</sup> An extensive theoretical study of the sol-gel transition phenomena was recently presented in Ref. 8 where many existing theoretical models and treatments were surveyed in details, showing that the pregel regime (or sol fraction) can be well accounted for with the use of a mean field approach. The original idea was first introduced by Flory<sup>9</sup> and Stockmayer<sup>10</sup> who assumed that all finite-size cluster associations in the system consist of tree-like branches only. The analytical extension of this approach to the postgel regime, where gel fraction appears, gives the classical theory of gelation now widely accepted.<sup>11</sup> The sol-gel transition within the frame work of this type of theory demonstrates smooth transition between the two states in the thermodynamic behavior, without any singularities typical in terms of phase transitions.

However, as was first discussed in Ref. 12, it is important to include the possibility of formation of closed cycles in the model, in order to describe an infinitely large cluster properly. As the result of such inclusion, the sol-gel transition has the characteristics of a first-order thermodynamic phase transition.<sup>8</sup>

Phase behavior of associating polymer solutions was the target of these studies and no attention has been paid to their interfacial properties. In the present paper we study the interfacial properties related to the region between the two coexisting phases of associating molecules. As a simple model system we take the system of  $f$ -functional monomers, each carrying  $f$  functional groups  $A$  that can react with each other forming reversible chemical

bonds  $A - A$  (see Fig. 1a). To obtain the free energy of this model system we use the classical density functional description which deals with tree-like clusters only (see Fig. 1b). The paper is organized as follows. In Section 2 we give an explicit expression for the free energy functional of inhomogeneous solution of tree-like associating molecules. In Section 3 we describe the analytical and numerical procedures for minimization of the free energy functional and derive the expression for the interfacial tension. Readers who are not interested in technical details might skip sections 2 and 3, and go to section 4 directly where we discuss the obtained results.

## 2. Free energy of an inhomogeneous system within the functional density approach

Consider a solution of  $f$ -functional monomers distributed in space with a nonuniform monomer density  $\rho(\mathbf{r})$ . The free energy of this system can be divided into two parts<sup>13</sup>

$$F([\rho(\mathbf{r})], T) = F^*([\rho(\mathbf{r})], T) + F_{str}([\rho(\mathbf{r})], T), \quad (1)$$

where the first term on the right-hand side contains the contribution from the excluded-volume interaction between monomer units and the second term is related to the structural free energy of the system of an ideal solvent. The excluded-volume interaction, in particular, can be accounted for by the following expression, which was proposed by Flory<sup>14</sup> based on a lattice model consideration,

$$F^*([\rho(\mathbf{r})], T) = \frac{T}{v} \int \left\{ [1 - v\rho(\mathbf{r})] \ln[1 - v\rho(\mathbf{r})] - \chi v^2 \rho^2(\mathbf{r}) \right\} d\mathbf{r}, \quad (2)$$

where  $T$  is the temperature of the system in  $k_B$  units,  $v$  is the volume of one lattice cell (the volume of one monomer) and  $\chi$  is the Flory-Huggins constant, with  $\chi T$  being the energy gain per monomer-monomer contact.

Our main purpose in this section is to introduce the structural term  $F_{str}([\rho(\mathbf{r})], T)$  as derived within the density functional approach in Ref. 12,15. Assuming that the average distance  $r_0$  between monomers is much less than the average length  $a$  of a chemical bond  $A - A$ ,

$$r_0 \ll a, \quad (3)$$

we write the structural free energy in the form

$$F_{str}([\rho(\mathbf{r})], T)/T = -S_{id}[\rho(\mathbf{r})] + \min\{S_{comb}[\rho(\mathbf{r}), \rho_A(\mathbf{r})] - S_A[\rho_A(\mathbf{r})]\}. \quad (4)$$

Here the first term

$$S_{id}[\rho(\mathbf{r})] = - \int \rho(\mathbf{r}) \ln \left( \frac{v\rho(\mathbf{r})}{f!} \right) d\mathbf{r} \quad (5)$$

corresponds to the translational entropy of the monomer units in space. The minimum of the second term is considered in the configurational space of all possible density distributions  $\rho_A(\mathbf{r})$ . We also have

$$S_{comb}[\rho(\mathbf{r}), \rho_A(\mathbf{r})] = - \int f\rho(\mathbf{r}) [\Gamma(\mathbf{r}) \ln(\Gamma(\mathbf{r})) + (1 - \Gamma(\mathbf{r})) \ln(1 - \Gamma(\mathbf{r}))] d\mathbf{r}, \quad (6)$$

where  $\Gamma(\mathbf{r}) \equiv \rho_A(\mathbf{r})/f\rho(\mathbf{r})$  is the local content of conversion, corresponding to the entropy of selecting reacted functional groups distributed with the density  $\rho_A(\mathbf{r})$ .

The other term in eq. (4),  $S_A$ , corresponds to the entropy of thermoreversible chemical bonds. Here we assume that under condition (3)  $S_A$  depends only on the density of reacted functional groups and it does not depend on a particular monomer structure. Thus  $S_A$  can be calculated for the simplest system of fully reacted monofunctional units. From Appendix A we have:

$$S_A[\rho_A(\mathbf{r})] = \int \frac{\rho_A(\mathbf{r})}{2} \ln \left[ \frac{\rho_A(\mathbf{r})(\hat{g}\psi)(\mathbf{r})}{e\psi(\mathbf{r})} \right] d\mathbf{r}, \quad (7)$$

where  $\rho_A(\mathbf{r})$  and  $\psi(\mathbf{r})$  are dependent equation

$$\rho_A(\mathbf{r}) = \psi(\mathbf{r})(\hat{g}\psi)(\mathbf{r}) = \psi(\mathbf{r}) \int g(\mathbf{r} - \mathbf{r}') \psi(\mathbf{r}') d\mathbf{r}' \quad (8)$$

with  $g(\mathbf{r})$  being the statistical weight of a bond with length  $\mathbf{r}$ . For a homogeneous system we can rewrite eq. (7) in the form

$$S_A(V, \rho_A) = V \frac{\rho_A}{2} \ln \frac{k\rho_A}{e} \quad (9)$$

where

$$k = \int g(\mathbf{r}) d\mathbf{r}. \quad (10)$$

The association caused contribution (9) was also obtained by Semenov and Rubinstein in Ref. 6 who considered the homogeneous systems only. After minimization of the second term in eq. (4) we recover the expression which is widely used to consider phase behavior of associating polymer systems

$$F_{str}^{hom}(T, V, \rho)/(TV) = \rho \ln \left( \frac{f!v\rho}{e} \right) + f\rho \left( \frac{\Gamma}{2} + \ln(1 - \Gamma) \right), \quad (11)$$

and

$$fk\rho = \frac{\Gamma}{(1 - \Gamma)^2}. \quad (12)$$

We shall not discuss details of phase behavior in this paper, but would like to mention that for certain values of parameters  $\chi$  and  $g$  it is more preferable for the system to be separated into two macroscopic sol phases with respectively different densities of monomers  $\rho_1$  and  $\rho_2$  which could be obtained from the equations

$$\mu_1(T, \rho_1) = \mu_2(T, \rho_2) \quad (13)$$

$$\pi_1(T, \rho_1) = \pi_2(T, \rho_2) \quad (14)$$

where  $\mu_i$  and  $\pi_i$  are the chemical potential and osmotic pressure of phase  $i$  ( $i = 1, 2$ ). We should also point out that if the density of monomers in the phase exceeds the critical value  $\rho^*$

$$fk\rho^* = \frac{f - 1}{(f - 2)^2} \quad (15)$$

then the gel phase (infinitely large network) will be formed.

In the next section we consider only the systems where two sol phases with different densities are present, describe the procedure that minimizes free energy functional (1), and derive the expression for the interfacial tension between the coexisting phases.

### 3. Minimization of the free energy functional and the interfacial tension

In order to proceed further, we introduce a coordinate system so that the  $z = 0$  surface coincides with the flat interface separating the two sol phases. For a density variation whose typical correlation length is much greater than the basic Kuhn length associated with a single bond, the operator  $\hat{g}$  can be approximated<sup>17</sup>

$$\hat{g} = k \left( 1 + \frac{a^2}{6} \frac{d^2}{dz^2} \right), \quad (16)$$

where the chemical equilibrium constant  $k$  is defined in eq. (10) and  $a$  is the average length of a chemical bond. The free energy per unit surface can then be expressed as

$$\frac{F}{S} = \frac{T}{v} \min \left\{ \int_{-L_1}^{L_2} \mathcal{F}(\phi(z), \phi_A(z), \dot{\phi}_A(z)) dz \right\} \quad (17)$$

where  $S$  is the area of the interface,  $L_1$  and  $L_2$  are the linear dimensions of each phase normal to the interface,  $\phi = v\rho$  is the volume fraction of monomers and we will refer to  $\phi_A = v\rho_A$  as the volume fraction of reacted functional groups. The dot symbol represents the derivative with respect to  $z$

$$\dot{\phi}_A \equiv \frac{d\phi_A}{dz}. \quad (18)$$

The density free energy  $\mathcal{F}$ , which is a functional of the local volume fractions of monomers and reacted functional groups, takes the form

$$\mathcal{F}(\phi, \phi_A, \dot{\phi}_A) = \mathcal{F}_{bls}(\phi) + \mathcal{F}_{comb}(\phi, \phi_A) + \mathcal{F}_A(\phi_A, \dot{\phi}_A). \quad (19)$$

The first term in (19) corresponds to the free energy of the broken-link system

$$\mathcal{F}_{bls}(\phi) = \phi \ln \phi + (1 - \phi) \ln(1 - \phi) - \chi \phi^2, \quad (20)$$

the second term in (19) is simply combinatorial

$$\mathcal{F}_{comb}(\phi, \phi_A) = f\phi \left( \Gamma \ln \Gamma + (1 - \Gamma) \ln(1 - \Gamma) \right), \quad \Gamma = \frac{\phi_A}{f\phi}, \quad (21)$$

and the third one corresponds to the entropy of the chemical bonds

$$\mathcal{F}_A(\phi_A, \dot{\phi}_A) = -\frac{\phi_A}{2} \ln \frac{g\phi_A}{e} + \frac{a^2 \dot{\phi}_A^2}{48 \phi_A} \quad (22)$$

where we have introduced a dimensionless chemical reaction constant

$$g = k/v. \quad (23)$$

While the free energy across the interface is given by eq. (17), the surface tension is defined through considering the excess free energy in reference to the bulk phases. We can then write

$$\sigma = \frac{T}{v} \min \left\{ \int_{-L_1}^0 (\mathcal{F}(\phi, \phi_A, \dot{\phi}_A) - \mathcal{F}_1^{hom}) dz + \int_0^{L_2} (\mathcal{F}(\phi, \phi_A, \dot{\phi}_A) - \mathcal{F}_2^{hom}) dz \right\} \quad (24)$$

where the terms

$$\begin{aligned} \mathcal{F}_i^{hom} \equiv \mathcal{F}^{hom}(\phi_i) &= \mathcal{F}_{sbl}(\phi_i) + f\phi_i \left( \frac{\Gamma_i}{2} + \ln(1 - \Gamma_i) \right) \\ fg\phi_i &= \frac{\Gamma_i}{(1 - \Gamma_i)^2} \quad (i = 1, 2), \end{aligned} \quad (25)$$

are simply free energies of two homogenous phases with monomer volume fractions  $\phi_1$  and  $\phi_2$  respectively on the left and right sides of the interface.

The minimization of the functional (24) is considered with the constraint

$$\int_{-L_1}^0 (\phi(z) - \phi_1) dz + \int_0^{L_2} (\phi(z) - \phi_2) dz = 0 \quad (26)$$

and the volume fractions  $\phi_1$  and  $\phi_2$  are obtained from eqs. (13), (14), or, written more explicitly,

$$\left. \frac{\partial \mathcal{F}^{hom}}{\partial \phi} \right|_{\phi=\phi_1} = \left. \frac{\partial \mathcal{F}^{hom}}{\partial \phi} \right|_{\phi=\phi_2} \quad (27)$$

$$(\phi_1 - \phi_2) \left. \frac{\partial \mathcal{F}^{hom}}{\partial \phi} \right|_{\phi=\phi_1} = \mathcal{F}_1^{hom} - \mathcal{F}_2^{hom} \quad (28)$$

Since any contributions to the free energy density which are independent of  $\phi$ , or linear in  $\phi$ , could be dropped or added,<sup>1</sup> we can introduce a new free energy density function  $\tilde{\mathcal{F}}(\phi, \phi_A, \dot{\phi}_A)$ ,

$$\tilde{\mathcal{F}}(\phi, \phi_A, \dot{\phi}_A) = \mathcal{F}(\phi, \phi_A, \dot{\phi}_A) + A\phi + B \quad (29)$$

where the parameters  $A$  and  $B$  are to be determined from equations

$$\mathcal{F}_1^{hom} + A\phi_1 + B = 0 \quad (30)$$

$$\mathcal{F}_2^{hom} + A\phi_2 + B = 0 \quad (31)$$

We can now rewrite eq. (24) in the form

$$\sigma = \frac{T}{v} \min \left\{ \int_{-\infty}^{+\infty} \tilde{\mathcal{F}}(\phi, \phi_A, \dot{\phi}_A) dz \right\} \quad (32)$$

where we have rewritten the integration limits in terms of infinity since  $\tilde{\mathcal{F}}$  approaches zero far from the interface.

According to a standard minimization procedure we introduce two Euler's equations

$$\frac{\partial \tilde{\mathcal{F}}}{\partial \phi} = 0 \quad (33)$$

$$\frac{\partial \tilde{\mathcal{F}}}{\partial \phi_A} - \frac{d}{dz} \frac{\partial \tilde{\mathcal{F}}}{\partial \dot{\phi}_A} = 0 \quad (34)$$

As the function  $\tilde{\mathcal{F}}$  is independent of  $z$ , a first integral can be used to replace eq. (34):

$$\tilde{\mathcal{F}} - \dot{\phi}_A \frac{\partial \tilde{\mathcal{F}}}{\partial \dot{\phi}_A} = 0. \quad (35)$$

From eq. (33)

$$\frac{\partial \mathcal{F}_{bls}}{\partial \phi} + A + f \ln(1 - \Gamma) = 0 \quad (36)$$

one can find the equilibrium profile of conversion  $\Gamma$

$$\Gamma(\phi) = 1 - \exp \left( -\frac{1}{f} \frac{\partial \mathcal{F}_{bls}}{\partial \phi} - \frac{A}{f} \right). \quad (37)$$

This expression is valid across the entire interface and it gives a relation between conversion  $\Gamma$  and monomer volume fraction  $\phi$ .

From eq. (35) it follows that

$$\frac{a^2 \dot{\phi}_A^2}{48 \phi_A} = \mathcal{F}_{bls} + A\phi + B + f\phi(\Gamma \ln \Gamma + (1 - \Gamma) \ln(1 - \Gamma)) - \frac{\phi_A}{2} \ln \frac{g\phi_A}{e} \quad (38)$$



Taking into account eq. (38) and the definition of  $\Gamma$  (see eq. (21)) we can now rewrite eq. (24) for the interfacial tension

$$\sigma = \frac{2T}{v} \int_{-\infty}^{+\infty} \mathcal{F}_\sigma(\phi(z)) dz, \quad (39)$$

where

$$\mathcal{F}_\sigma(\phi) = \mathcal{F}_{bs}(\phi) + A\phi + B + f\phi \left( \frac{\Gamma(\phi)}{2} \ln \frac{e\Gamma(\phi)}{fg\phi(1-\Gamma(\phi))^2} + \ln(1-\Gamma(\phi)) \right) \quad (40)$$

Furthermore,  $\dot{\phi}(z)$  can be written as

$$\dot{\phi}_A = f(\dot{\phi}\Gamma + \phi\dot{\Gamma}) = f\dot{\phi} \left( \Gamma + \phi \frac{\partial \Gamma}{\partial \phi} \right) \quad (41)$$

Finally, with the help of eqs. (38) and (40),  $\phi(z)$  obeys a simple differential relation

$$\dot{\phi}^2 = \frac{48}{a^2} \frac{\phi \Gamma \mathcal{F}_\sigma}{f \left( \Gamma + \phi \frac{\partial \Gamma}{\partial \phi} \right)^2} \quad (42)$$

where

$$\frac{\partial \Gamma}{\partial \phi} = \frac{1}{f} \frac{\partial^2 \mathcal{F}_{bs}}{\partial \phi^2} (1 - \Gamma). \quad (43)$$

Therefore, the volume fraction profile  $\phi(z)$  can be obtained using the simple iterative numerical procedure

$$\phi(z_{i+1}) = \phi(z_i) + \dot{\phi}(\phi(z_i))(z_{i+1} - z_i) \quad (44)$$

where  $\dot{\phi}(\phi)$  is defined by eq. (42). The interfacial tension  $\sigma$  can then be easily found through eq. (39) after the calculation of the density.

## 4. Results and discussions

In this paper we study the temperature dependence of the interfacial tension in the solution of associating monomers capable of forming thermoreversible chemical bonds with each other. The functionality  $f$  of a monomer unit defines the structure of associations that could be

formed . If  $f = 2$  then the system would contain linear molecules of various lengths. For  $f = 3$  more complex structures could be formed as shown in Figure 1.

The temperature dependence of the Flory parameter  $\chi$  is considered to have the simple form

$$\chi = \frac{\theta}{2T}, \quad (45)$$

although more exotic temperature dependence could be introduced. We also introduce parameter  $g$  defined through eq. (23) in the form

$$g = g_0 \exp(-E\chi), \quad (46)$$

where  $g_0$  is the chemical reaction constant at high temperatures and  $E\theta/2$  is the energy of a chemical bond formed between two functional groups.

As the first step, we consider the interfacial tension in a system of bi-functional units ( $f = 2$ ). If the chemical reaction constant  $g$  is high enough then all functional groups would be reacted and the system would contain one infinitely large linear chain. In this limiting case our theory should recover the treatment for the interfacial tension proposed by Helfand and Tagami<sup>18,19</sup>. Writing free energy of the solution containing infinitely long linear chain in the form<sup>20</sup>

$$F = \frac{T}{v} \int \left[ \frac{a^2}{24} \frac{(\nabla\phi)^2}{\phi} + (1 - \phi) \ln(1 - \phi) + \chi\phi(1 - \phi) \right] d\mathbf{r} \quad (47)$$

one could obtain the expression for the interfacial tension  $\sigma_0$  corresponding to the case where the rich phase (containing all chain monomers) and poor phase (only solvent molecules) are independently formed

$$\sigma_0 = \frac{Ta}{v\sqrt{6}} \int_0^{\phi_0} \left( \frac{1 - \phi}{\phi} \ln(1 - \phi) + \chi(1 - \phi) - \mu_0 \right)^{1/2} d\phi \quad (48)$$

Here  $T\mu_0$  is the chemical potential and  $\phi_0$  is the volume fraction of monomers in the rich phase. These two parameters could be found from the equations

$$\mu_0 = \chi(1 - 2\phi_0) - \ln(1 - \phi_0) - 1 \quad (49)$$

$$\mu_0\phi_0 = \chi\phi_0(1 - \phi_0) + (1 - \phi_0) \ln(1 - \phi_0) \quad (50)$$

which balance chemical potentials and osmotic pressures of bi-functional monomer units in the poor and rich phases.

Figure 2 shows the temperature dependence of interfacial tension  $\sigma_0$  given by eq. (48) (open circles) together with  $\sigma$  based on eq. (39) for  $E = 0$  and different values of interaction parameters  $g_0$  introduced in eq. (46). For large  $g_0$  ( $\ln g_0 = 20$ , dotted line) we see that our result agrees exactly with the Helfand-Tagami theory thus confirming the model in the ( $f = 2, g \gg 1$ ) limit.

Our model also accounts for the situation where a polydispersed system of linear chains system can be formed for smaller  $g_0$ . For smaller values of  $g_0$  ( $\ln g_0 = 2$ , dashed line, and  $\ln g_0 = 0$ , solid line) when the reaction of functional groups is incomplete one can see the singularities that might occur in the  $\sigma(T)$  behavior. Distinct singularity points can be identified where sudden changes in curvatures occur.

Figure 3 demonstrates the interfacial tension of the  $f = 3$  case where the branched associates may coexist across the interface and one can also observe the similar singularity behavior for  $\sigma(T)$ .

The described types of singularities in the interfacial tension behavior arise due to the singularities that can occur in the behavior of the density profiles  $\phi(z)$  and  $\phi_A(z)$  along the interface (smooth profiles without any singularities are shown at the top of Fig. 4). For a certain value of parameters  $\chi$  and  $g$  one can expect a sudden change in the slope of  $\phi_A(z)$  as shown in Fig. 5. This picture is observed if  $\Gamma + \phi \partial\Gamma/\partial\phi$  introduced in eq. (42) becomes negative in the interval  $(\phi', \phi'')$  as shown at the bottom of Fig. 5. According to eq. (41) the slope of  $\phi(z)$  becomes infinite at  $z'$  and  $z''$  which correspond to  $\phi'$  and  $\phi''$  and the slope of  $\phi_A(z)$  is negative in the entire interval  $(z', z'')$ .

The more complex behavior is observed when the equilibrium conversion  $\Gamma(\phi)$  defined by eq. (37) becomes negative, as shown at the bottom of Fig. 6 for the interval  $(\phi'', \phi''')$ . Physically  $\Gamma$  is a positive quantity and therefore the region  $(\phi'', \phi''')$  should be skipped when calculating  $\sigma$  defined by (39). Skipping this  $(\phi'', \phi''')$  interval leads to the sudden jump of the volume fraction profile  $\phi(z)$  at the point  $z''$  as shown at the top of Fig. 6. Similar

noncontinuous behavior of polymer density was previously discussed in Ref. 21 where the authors considered a polymer globule formed by a long polymer chain with saturated physical bonds. This type of behavior could be explained as follows. As one goes across the interface (see the top of Fig. 6) the volume fraction  $\phi$  increases until it reaches the value  $\phi''$  at the point  $z''$ . At the same time the number of reacted functional groups (or reduced density of reacted functional groups  $\rho_A$ ) decreases and becomes infinitely small as  $\phi$  reaches  $\phi''$  (at this point conversion  $\Gamma$  is zero). The fact that  $\phi_A = 0$  ensures that there would be no loss of conformational entropy for the system associated with the jump of the volume fraction at the point  $z''$  because square gradient term (see eq. (22)) depends only on derivative of  $\phi_A$  which is continuous at this point.

Hence, the behavior of interfacial profile  $\sigma(T)$  shown in Figure 3 could be explained as follows. As the temperatures of the system decreases and reaches  $T_1$  the interface first appears and the interfacial tension starts to increase. As temperature reaches the value of  $T_2$  the change in the curvature of  $\sigma(T)$  profile is observed. This curvature change is connected to the appearance of the negative slope in the behavior of  $\phi_A(z)$  (as shown in Fig. 5). When the temperature of the system reaches  $T_3$  one observes the change in the slope of  $\sigma(T)$  profile due to the discontinuity of the monomer volume fraction  $\phi(z)$  (see Fig. 6) which first appears at this temperature.

## 5. Conclusion

In this paper, we analyze the interfacial structure and calculate the temperature dependence of the interfacial tension  $\sigma$  in associating solutions of  $f$ -functional monomers. We find that there are two types of singularities which occur in the behavior of the density profiles along the interface. At certain temperatures the density of reacted functional groups may decrease within some region inside the interface while the polymer density always increases. Also, the polymer density may exhibit a sudden jump at the point where the density of reacted functional groups becomes infinitely small. The first of these singularities leads to the change in the curvature of the  $\sigma(T)$  profile and the second one changes the slope of that profile.

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### A. Calculation of the entropy of thermoreversible chemical bonds<sup>12,15</sup>

In this Appendix we consider the system of fully reacted monofunctional monomers units. If  $\rho_A(\mathbf{r})$  is the monomer density, then the entropy of chemical bonds  $S_A$  is defined as follows

$$S_A[\rho_A(\mathbf{r})] = S_{pair}[\rho_A(\mathbf{r})] - S_{id}[\rho_A(\mathbf{r})]. \quad (\text{A1})$$

where  $S_{pair}$  is the entropy of dimers formed due to the associations and  $S_{id}$  defined by eq. (5) corresponding to the translational entropy of monomers. We assume that external field  $\varphi(\mathbf{r})$  produces an equilibrium density  $\rho_A(\mathbf{r})$ , and in the mean field approximation

$$TS_{pair}[\rho_A(\mathbf{r})] = E[\varphi(\mathbf{r})] - F_{pair}[\varphi(\mathbf{r})] \quad (\text{A2})$$

Here  $E[\varphi(\mathbf{r})]$  and  $F_{pair}[\varphi(\mathbf{r})]$  are the energy and free energy of dimers in the field  $\varphi(\mathbf{r})$  respectively. They satisfy the following expressions<sup>17</sup>

$$E[\varphi(\mathbf{r})] = \int \rho_A(\mathbf{r})\varphi(\mathbf{r})d\mathbf{r} \quad (\text{A3})$$

$$F_{pair}[\varphi(\mathbf{r})] = -T \ln \left[ \frac{\left( \int \psi(\mathbf{r})(\hat{g}\psi)(\mathbf{r})d\mathbf{r} \right)^N}{2^N N! v^{2N}} \right] \quad (\text{A4})$$

where  $N$  is the total number of dimers

$$N = \frac{1}{2} \int \rho_A(\mathbf{r})d\mathbf{r} \quad (\text{A5})$$

and

$$\psi(\mathbf{r}) = \exp \left( -\frac{\varphi(\mathbf{r})}{T} \right) \quad (\text{A6})$$

$$(\hat{g}\psi)(\mathbf{r}) = \int g(\mathbf{r} - \mathbf{r}')\psi(\mathbf{r}')d\mathbf{r}' \quad (\text{A7})$$

with  $g(\mathbf{r})$  corresponding to the statistical weight of a bond with length  $\mathbf{r}$ . According to general thermodynamic relations<sup>16</sup> the density of functional groups can be written as

$$\rho_A(\mathbf{r}) = \frac{\delta F_{pair}[\varphi(\mathbf{r})]}{\delta \varphi(\mathbf{r})} = 2N \frac{\psi(\mathbf{r})(\hat{g}\psi)(\mathbf{r})}{\int \psi(\mathbf{r})(\hat{g}\psi)(\mathbf{r})} \quad (\text{A8})$$

Using eqs. (A5) and (A8) one can rewrite eq. (A4) in the form

$$F_{pair}[\varphi(\mathbf{r})] = -T \int \frac{\rho_A(\mathbf{r})}{2} \ln \left[ \frac{\psi(\mathbf{r})(\hat{g}\psi)(\mathbf{r})}{\rho_A(\mathbf{r})} \frac{e}{v^2} \right] d\mathbf{r} \quad (\text{A9})$$

Eliminating  $\varphi(\mathbf{r})$  from eq. (A3) with the help of eq. (A6) and substituting the result into eq. (A2) together with expression (A9) we obtain

$$S_{pair}[\rho_A(\mathbf{r})] = \int \frac{\rho_A(\mathbf{r})}{2} \ln \left[ \frac{(\hat{g}\psi)(\mathbf{r})}{\psi(\mathbf{r})\rho_A(\mathbf{r})} \frac{e}{v^2} \right] d\mathbf{r}, \quad (\text{A10})$$

and for the entropy of chemical bonds given by eq. (A1) we finally get

$$S_A[\rho_A(\mathbf{r})] = \int \frac{\rho_A(\mathbf{r})}{2} \ln \left[ \frac{\rho_A(\mathbf{r})(\hat{g}\psi)(\mathbf{r})}{e\psi(\mathbf{r})} \right] d\mathbf{r}, \quad (\text{A11})$$

which is the formula used in eq. (7).

## References and notes

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## Figure captions

**Figure 1.** Formation of a reversible chemical bond  $A - A$  between two three-functional monomers (a) and an example of a tree-like cluster formed by three-functional monomers (b).

**Figure 2.** Interfacial tension  $\sigma$  given by eq. (39) ( $v = 1, a = 1$ ) as a function of temperature for bi-functional units with  $f = 2$ ,  $E = 0$ , and different values of  $\ln g_0$ . Open circles correspond to the limited case given by eq. (48).

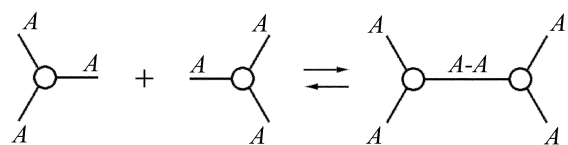
**Figure 3.** Interfacial tension  $\sigma$  given by eq. (39) ( $v = 1, a = 1$ ) as a function of temperature for three-functional units with  $f = 3$  and values of interaction parameters shown in the upper right corner.

**Figure 4.** Equilibrium profiles of volume fraction  $\phi$  (solid line) and volume fraction of reacted functional groups  $\phi_A$  (dash line) along the interface in the case of  $f = 3$  and values of interaction parameters shown in the upper right corner (top). Also shown are the equilibrium conversion  $\Gamma$  (solid line) and  $\Gamma + \phi \partial \Gamma / \partial \phi$  (dash line) as functions of volume fraction  $\phi$ .

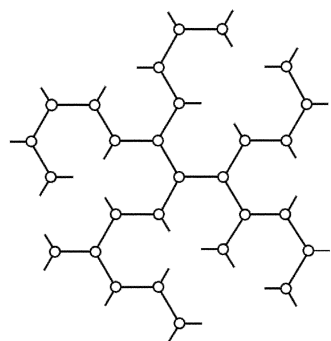
**Figure 5.** See caption for Fig. 4.

**Figure 6.** See caption for Fig. 4.

**Figure 1.** A.Ermoshkin, I.Erukhimovich, J.Chen

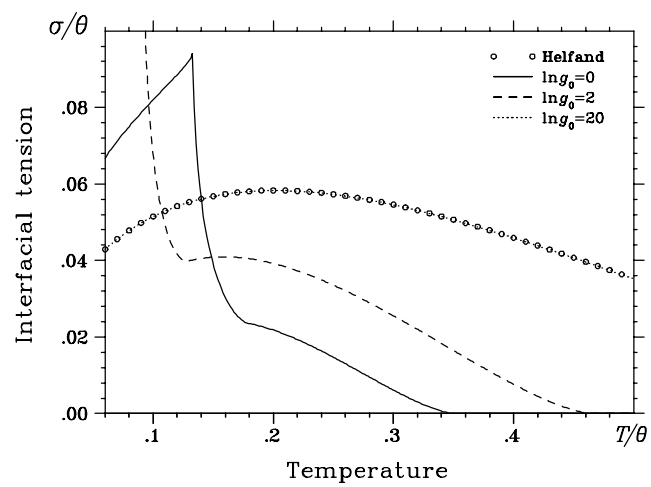


(a)

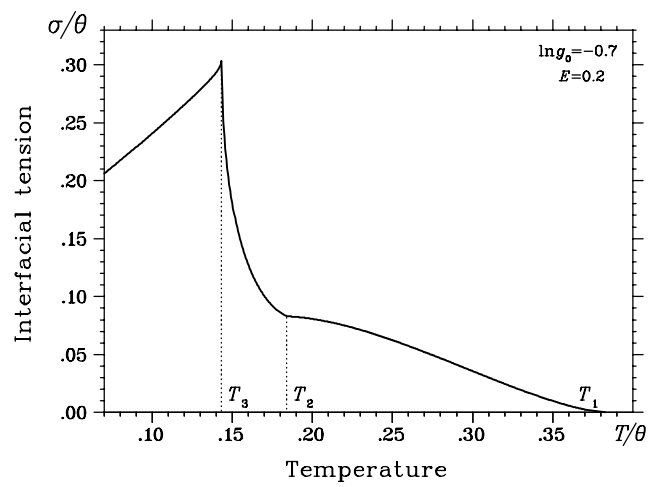


(b)

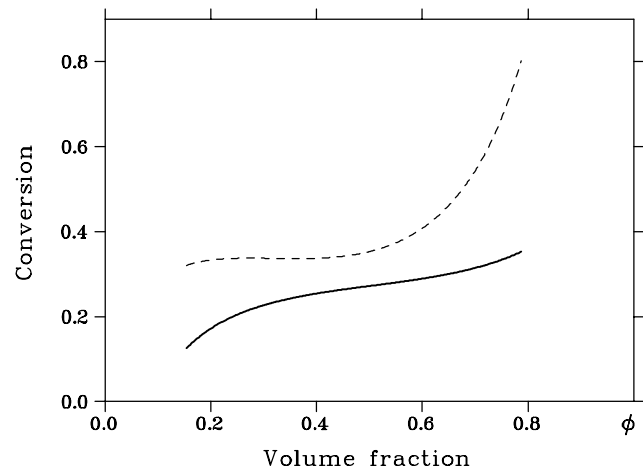
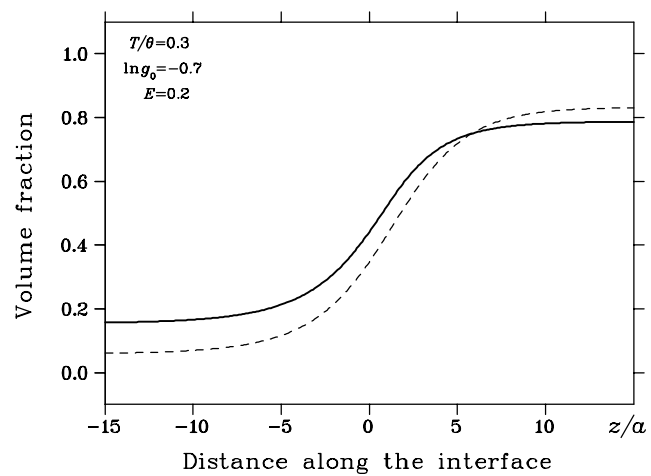
**Figure 2.** A.Ermoshkin, I.Eruehimovich, J.Chen



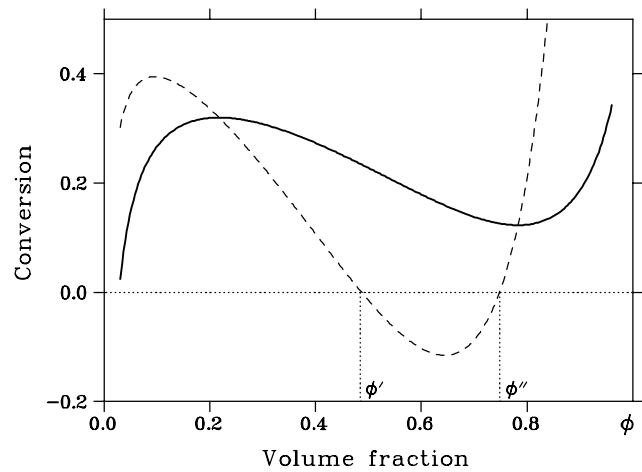
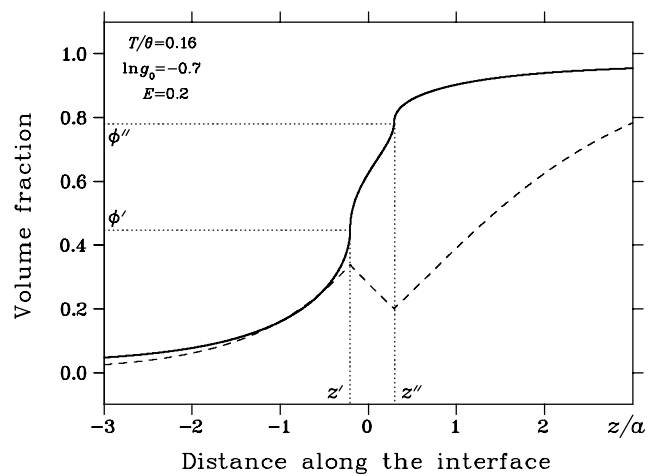
**Figure 3.** A.Ermoshkin, I.Erukhimovich, J.Chen



**Figure 4.** A.Ermoshkin, I.Erukhimovich, J.Chen



**Figure 5.** A.Ermoshkin, I.Erukhimovich, J.Chen



**Figure 6.** A.Ermoshkin, I.Erukhimovich, J.Chen

